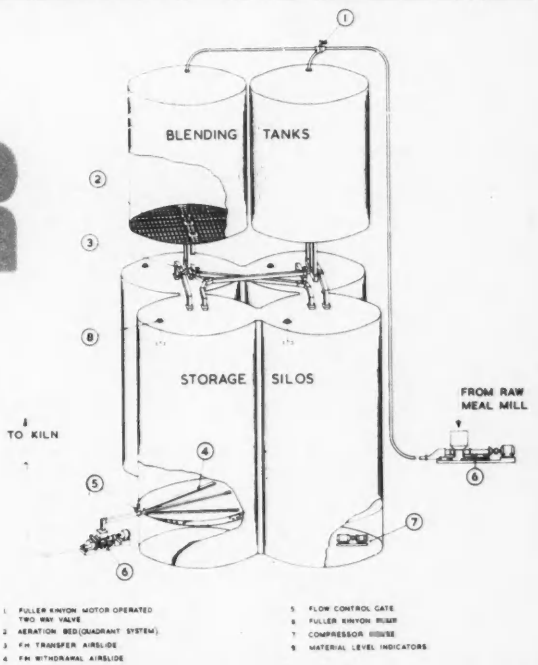
CEMENT AND LIME MANUFACTURE

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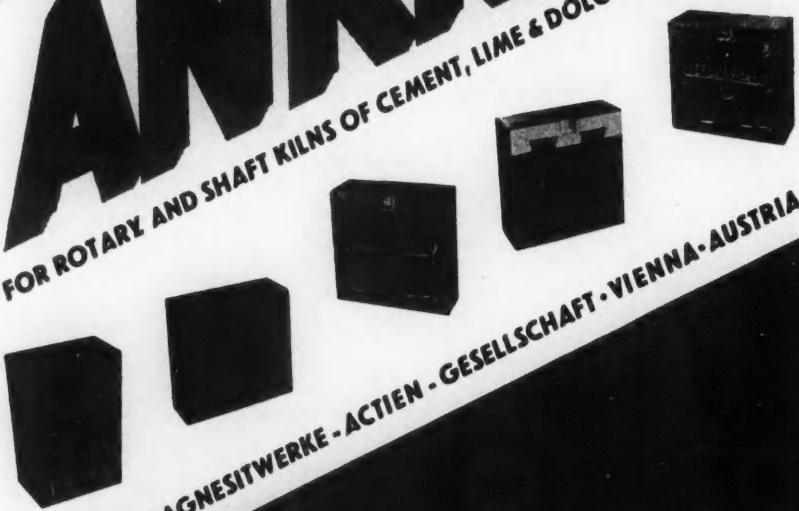
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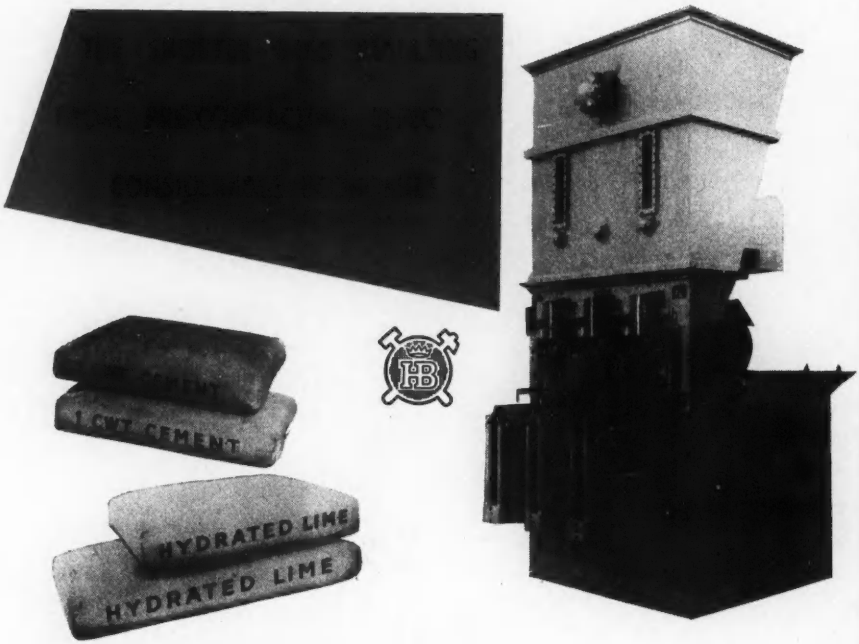
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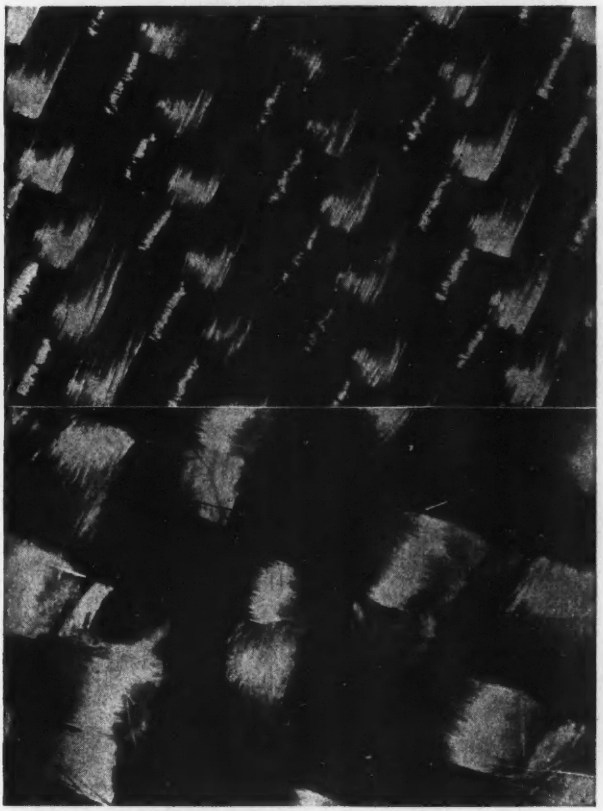
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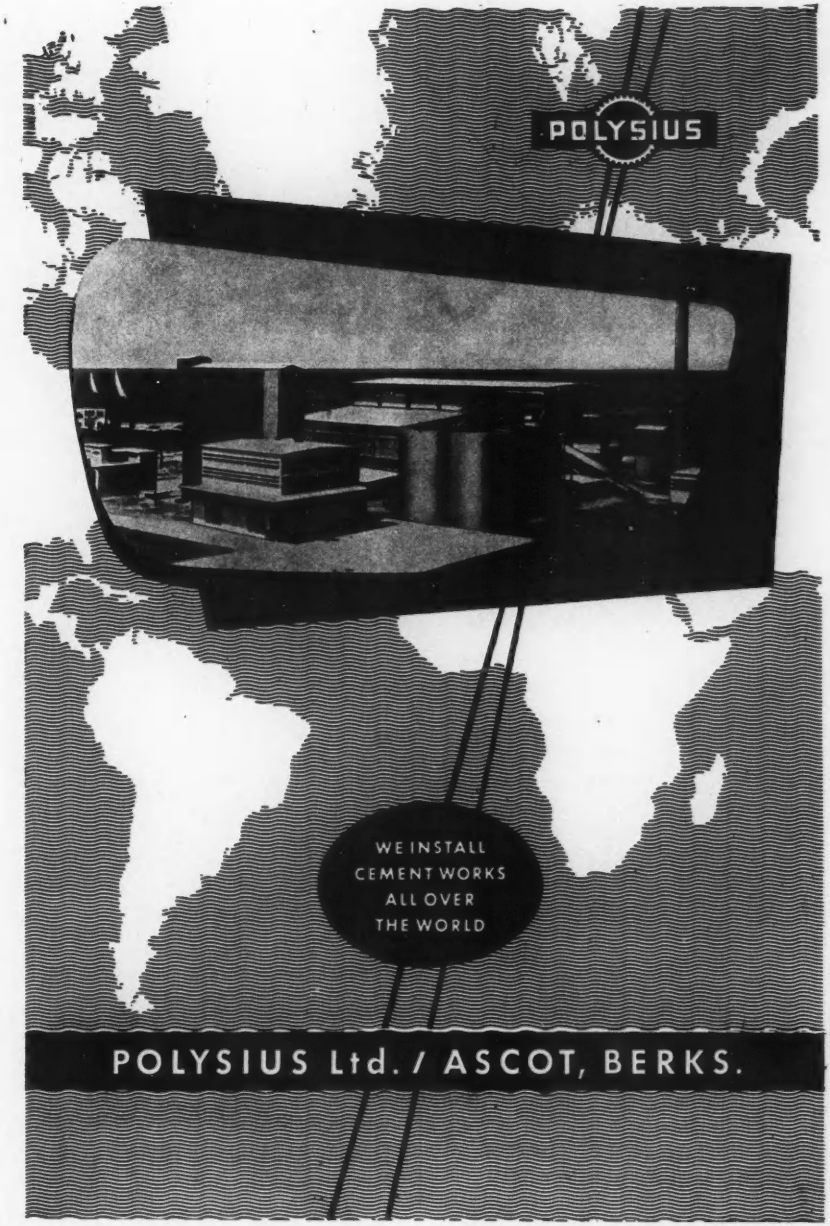


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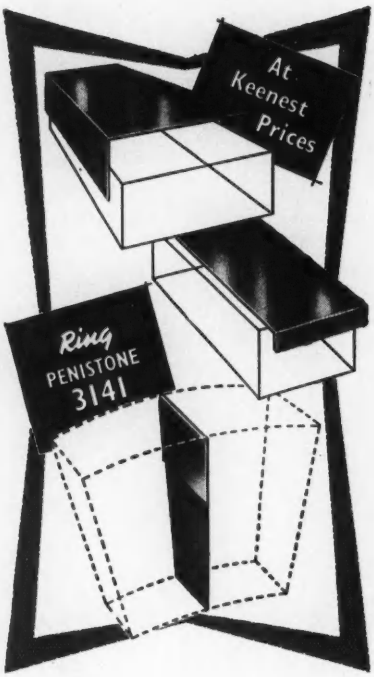
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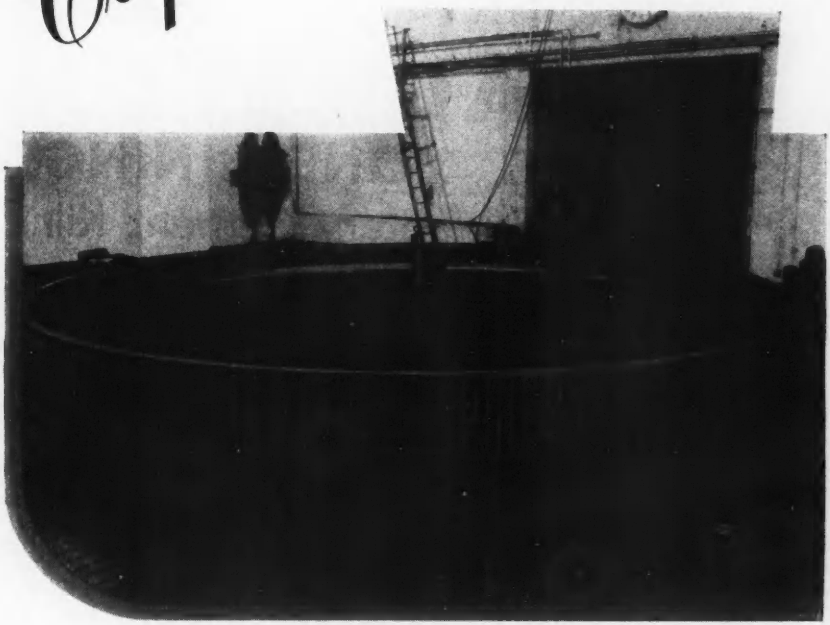
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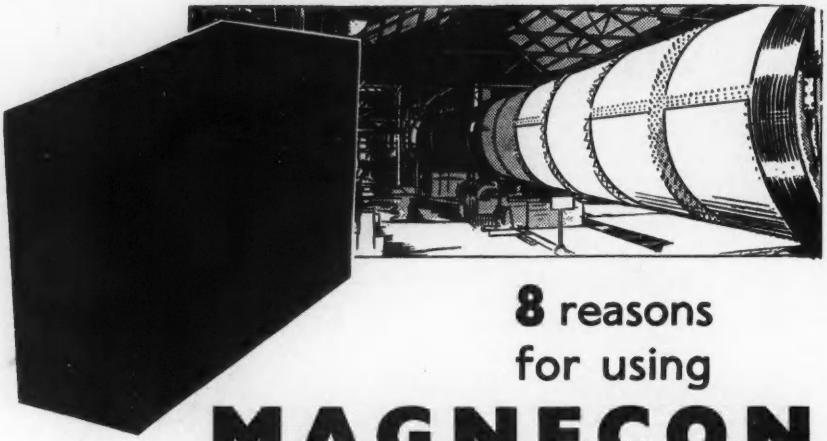
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VOLUME XXXII. NUMBER 1. JANUARY, 1959

Reaction of Portland Cement with Carbon Dioxide.

AN investigation made by Mr. Charles M. Hunt, Mr. Vernon Dantzler, Mr. Lewis A. Tomes, and Mr. Raymond L. Blaine at the U.S. National Bureau of Standards has confirmed that the reaction of Portland cement with carbon dioxide is greatly influenced by the moisture environment of the cement, and that reaction with carbon dioxide and water also affects the subsequent hydration of the cement. The following notes are taken from a report of the investigation printed in the Journal of the Bureau for May, 1958.

Samples of Portland cement were exposed to carbon dioxide at different relative humidities for different periods of time and analysed after exposure. At relative humidities of less than 25 per cent. carbonation was very slow, suggesting that the cement would not have reacted with much more carbon dioxide even if it were exposed for a much longer period. At relative humidities of 50 to 55 per cent. the rate of carbonation increased, and at humidities of 90 to 95 per cent. the increase was most marked and showed no evidence of ending after a week of exposure.

Because the rate of carbonation was so dependent on relative humidity, cement was also exposed by passing carbon dioxide into a freshly-mixed paste. The initial water-cement ratio of the paste was 0·5, but the mixture dried during exposure. During the first few hours the paste carbonated much faster than the cement, but thereafter the rate diminished sharply probably due to drying of the paste. It is clear that water is an important limiting factor in the rate of carbonation of cement.

Cement, and fresh cement paste, were also exposed to air. Again the fresh paste acquired much more carbon dioxide than the dry cement during the first day, but, after drying, the rate for paste was slightly less than that for cement. From these results it is clear that, even at the low carbon dioxide concentrations normally present in air, water can also be a rate-determining factor.

The cement contained more carbon dioxide after a week in air than in dry carbon dioxide. Also, the cement paste contained more carbon dioxide after a

week's exposure to air than was present in dry cement after a similar period in carbon dioxide at 50 to 55 per cent. relative humidity. It is therefore concluded that the concentration of water can exert a greater effect on the rate of carbonation than the concentration of carbon dioxide.

Cements containing different amounts of carbon dioxide were mixed with water and allowed to hydrate. Non-evaporable water in the hardened paste was determined after one day, seven days, and twenty-eight days of hydration. The results showed that the more highly-carbonated cements contained smaller amounts of non-evaporable water after hydration. There was no simple stoichiometric relationship between the increase in carbon dioxide content of the cement and the decrease in non-evaporable water in the paste, but comparatively small differences in the number of millimoles of carbon dioxide in the cement were associated with rather large differences in the number of millimoles of non-evaporable water. The effect was just as evident after twenty eight days of hydration as after the first day.

Pastes were prepared of four specimens of cement in which the initial water content varied from specimen to specimen, whereas the carbon dioxide content was nearly constant. These were compared with pastes of four specimens in which both carbon dioxide and water contents of the original cement varied from specimen to specimen. It was evident that both the water and carbon dioxide in the original cement had an influence on subsequent hydration. The comparative effects of the water and carbon dioxide in the original cement can perhaps be best illustrated by considering the non-evaporable water content of the hydrated paste as a function of the water content of the original cement; it was seen that carbon dioxide produced an effect on hydration additional to that produced by water in the original cement. The decrease in millimoles of non-evaporable water in the paste was also somewhat greater than the total number of millimoles of carbon dioxide and water in the cement that were associated with the effect.

Cement in a fresh paste is particularly susceptible to carbonation wherever the surface is exposed. The results gave no direct evidence about the quality of the cement after carbonation, but they showed that the exposed surface of freshly-mixed cement would react with carbon dioxide many times as fast during the first few hours as would the same cement before mixing. It was also evident that the amount of non-evaporable water in a hydrated cement after a given time of hydration was influenced to a measurable extent by the amount of carbon dioxide in the original cement before mixing.

The mechanism by which carbonation and reaction with atmospheric moisture reduces subsequent hydration was not established. The similarity of the effect at all ages suggests that changes produced during carbonation do not affect the rate of hydration as such, except possibly within the first few hours. However, as a result of carbonation, a fraction of the cement is made unavailable for hydration, and the amount of hydratable material so affected is not a linear function of carbon dioxide content. From the standpoint of practical use it is doubtful if small amounts of carbon dioxide and water seriously impair the hydraulic properties of Portland cement.

Tests on Portland Blastfurnace Cement in Poland.

IN the year 1951 the results of tests made in Poland on a mixture comprising 50 per cent. of ordinary Portland cement and 50 per cent. of blastfurnace slag were reported in "Cement-Wapno-Gips." It was found that the strength at 28 days of the Portland cement alone was 5,490 lb. per square inch, and of the Portland-blastfurnace cement 6,820 lb. per square inch. The results of more recent tests are given by K. Cichon and S. Stolinski in a recent number of the

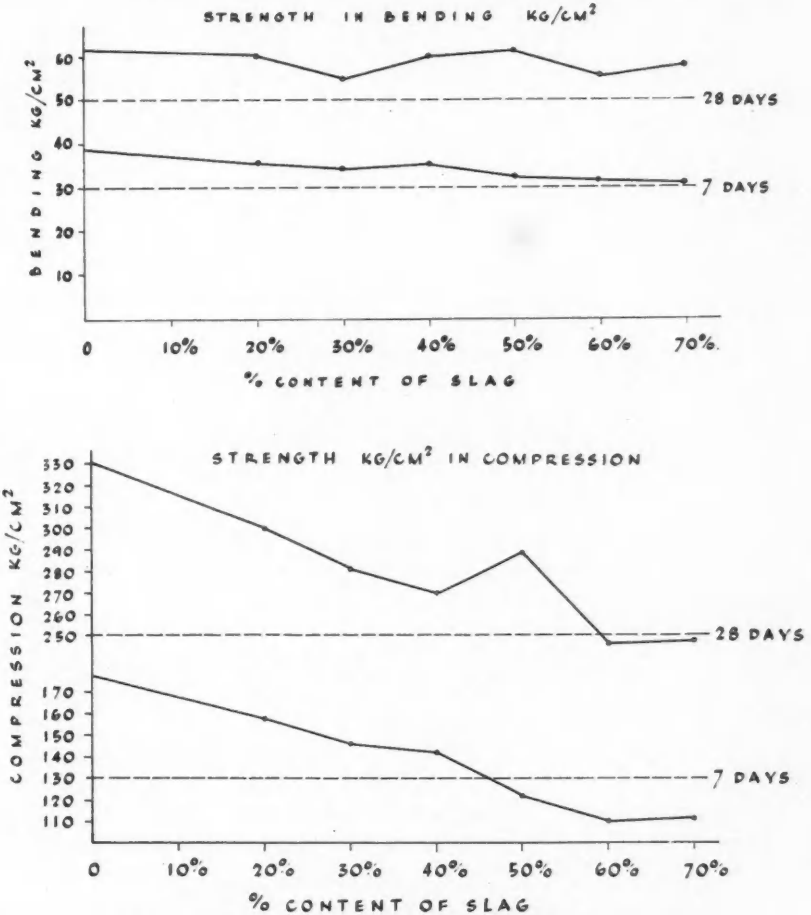


Fig.1.—Properties of blastfurnace cement made with slag from the Zawiercie Steel Works.

same journal, from which the following is abstracted. The composition and properties of the cement used in the earlier tests were as follows.

Portland cement.—Heat losses, 1·16 per cent.; SiO_2, 23·58 per cent.; R_2O_3, 7·80 per cent.; CaO, 64·80 per cent.; MgO, 1·20 per cent.; SO_3, 1·24 per cent. Bending strength at seven days, 664 lb. per square inch; at 28 days, 1,038 lb. per square inch Compressive strength at seven days, 2,630 lb. per square inch; at 28 days, 5,490 lb. per square inch.

Blastfurnace slag.—Heat losses, 0·92 per cent.; SiO_2, 34·06 per cent.; R_2O_3, 13·12 per cent.; CaO, 45·32 per cent.; MgO, 6·48 per cent.

Portland-blastfurnace cement.—Heat losses, 0·76 per cent.; SiO_2, 28·11 per cent.; R_2O_3, 11·32 per cent.; CaO, 54·12 per cent.; MgO, 4·21 per cent.; SO_3,

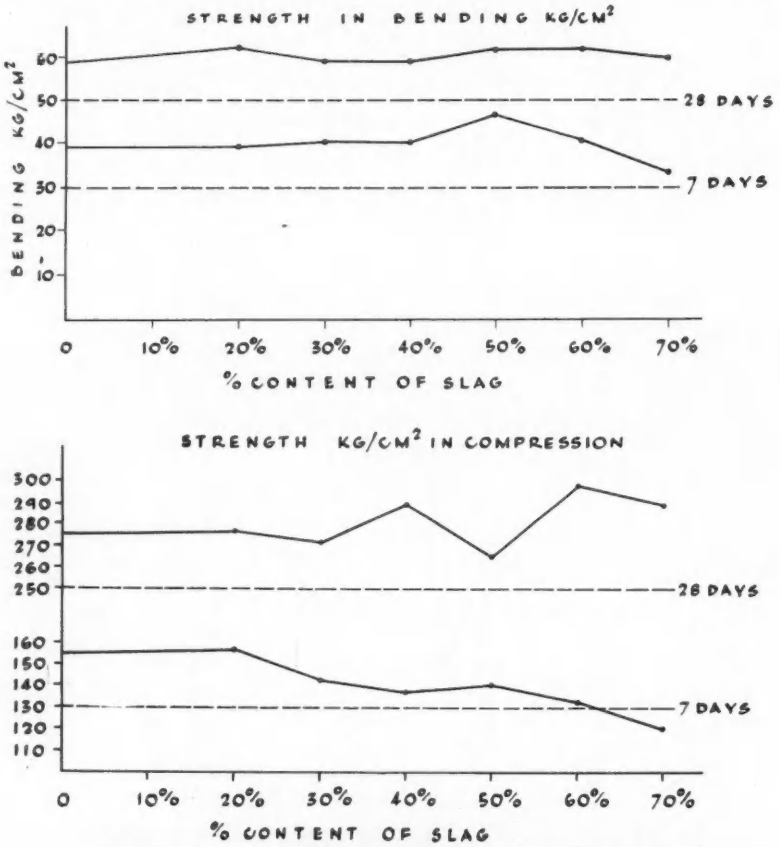


Fig.2.—Properties of blastfurnace cement made with slag from the Buczek Steel Works.

1·37 per cent. Bending strength at seven days, 730 lb. per square inch; at 28 days 1,055 lb. per square inch. Compressive strength at seven days, 2,790 lb. per square inch; at 28 days, 6,820 lb. per square inch.

In the later tests slags obtained from the Zawiercie and Buczek steelworks were used, the proportions varying from 20 per cent. to 70 per cent. The slag from the Zawiercie works had the following composition:

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} = 1{\cdot}03; \quad \frac{SiO_2}{Al_2O_3} = 3{\cdot}8.$$

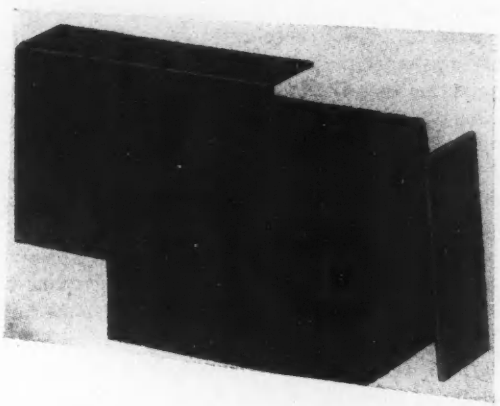
The corresponding data for the slag from the Buczek works are

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} = 0{\cdot}89; \quad \frac{SiO_2}{Al_2O_3} = 2{\cdot}2.$$

The slags were ground under laboratory conditions to the fineness of Portland cement; that is, to pass a sieve with 4,900 holes per square centimetre. The results of the tests are shown in *Figs.* 1 and 2.

New Jointing for Kiln Linings.

A new method of jointing kiln linings has been produced by Kaiser Aluminium & Chemical Sales, of Pittsburgh, U.S.A., and is stated to have given good results in long-period tests. A steel shim is bonded to one side of the block and bent



for a short distance over the exposed face. The shim does not reach to the back of the brick, so that it is not in contact with the shell of the kiln and does not transmit heat to the shell. When the kiln is fired the part of the shim on the face of the block oxidises and combines with the clinker to form a tight protective coating. The layer of adhesive which bonds the shim to the brick melts when the kiln is fired, permitting circumferential expansion. A cardboard strip is also bonded to the end of the brick to permit longitudinal expansion.

It is stated that if these blocks are used the time required to line a kiln may be reduced by up to 50 per cent.

Standards for Special Cements.

IN the year 1955 the Cement Statistical & Technical Association (Cembureau), of Malmö, Sweden, issued a book containing the essential details of all the specifications for Portland cement published throughout the world. This is now supplemented with " Review of Standards for Cements other than Portland " (price 30s.), which gives the principal requirements of the specifications of various countries for blastfurnace, supersulphated, pozzolanic, high-alumina, masonry, natural, mixed, and lime-blastfurnace and lime-pozzolanic cements. The work is printed in the English language, and units of measurement are given in metric and Imperial units. The work gives details relating to various qualities of these cements in accordance with the requirements of about eighty national standards. Some of these cements are briefly described as follows.

Supersulphated cement contains at least 75 per cent. blastfurnace slag, calcium sulphate, and at most 5 per cent. of lime, Portland-cement clinker, or Portland cement. The content of calcium sulphate expressed as sulphuric anhydride (SO_3) must be higher than 5 per cent. Supersulphated cement differs essentially from blastfurnace Portland cement in the relatively small percentage of Portland cement or lime and its increased resistance to sea-water and other aggressive agents.

Pozzolanic cements are produced by grinding Portland cement clinker and pozzolana with sufficient gypsum necessary to regulate the set. Pozzolana is, at ordinary temperatures and in the presence of moisture, capable of forming hydraulic compounds by reacting with the lime liberated during the hydration of cement. Natural pozzolanas are mostly of volcanic origin. Artificial pozzolanas are mainly obtained by heat treatment of materials such as clay, shale, siliceous rocks, and pulverised-fuel ash (fly ash). The characteristics of pozzolanic cements are low heat of hydration and high resistance to aggressive waters. As a rule, pozzolanic Portland cement has appreciably less strength than Portland cement at earlier ages, but this difference is less in course of time.

Mixed Portland cements are obtained by grinding a mixture of Portland cement clinker, a setting-time regulator, and an inert material as, for example, sand.

Lime-blastfurnace cements and lime-pozzolana cements are obtained by grinding a mixture of lime, granulated blastfurnace slag or pozzolana, and a setting-time regulator. These cements have lower strength than the corresponding blastfurnace or pozzolanic cement.

Natural cements are obtained by grinding calcined argillaceous limestone together with a setting-time regulator. The raw materials usually have a composition such that they are suitable without adjustment. Natural cement usually has low strength.

Masonry cements are based on Portland cement and contain one or more other materials which may be of a relatively inert nature and the purpose of which is to provide special properties, such as plasticity and water-retentivity.

Resistance of Portland Cement to Sulphates.

A COMMITTEE of the American Society for Testing Materials has supervised a series of tests made in various laboratories of a new method of determining the potential resistance of Portland cement to the action of sulphates, and is satisfied that it is satisfactory. The method, which is based on the expansion of bars of mortar containing a content of SO_3 equal to 7 per cent. of the weight of the cement, is described in full in a paper in a recent number of the journal of the Society.

APPARATUS.—(1) Scales and weights, conforming to Section 2(a) and (b) of the Standard Method of Test for Compressive Strength of Hydraulic Mortars (C 109). (2) Glass graduates of 250-ml. capacity, with graduations at 2-ml. intervals, for measuring the mixing water, made to deliver the indicated volume at 20 deg. C. (68 deg. F.). The main graduation lines are circles and are numbered. The least graduations extend at least one-seventh of the way around the cylinder and intermediate graduations at least one-fifth of the way around. Subdivisions may be omitted for the lowest 10 ml. (3) A tamper of non-absorptive and non-abrasive material such as medium-hard rubber or seasoned oak rendered non-absorptive by immersion for 15 minutes in paraffin at about 200 deg. C. (392 deg. F.) and having a cross section of ½ in. by 1 in., and of convenient length (5 in. or 6 in.). The tamping face is flat and at right angles to the length of the tamper. (4) A trowel with a steel blade 4 in. to 6 in. long with straight edges. (5) A mixer, bowl, and paddle, conforming to Section 2 of the Tentative Method for Mechanical Mixing of Hydraulic Cement Mortars of Plastic Consistency (C.305). (5) Moulds conforming to Section 2(c) of the Standard Method of Test for Autoclave Expansion of Portland Cement (C.151). (6) A length comparator, for measuring the length of the mortar bars, conforming to Section 2(*f*) of the Standard Method of Test for Autoclave Expansion of Portland cement (C.151).

MAKING THE TEST SPECIMENS.—The temperature of the air in the vicinity of the mixing is between 20 deg. C. and 27·5 deg. C. (68 deg. F. and 81·5 deg. F.). The temperature of the mixing water, the moist closet or room, and the water in the storage tank, must not vary from 23 deg. C. (73·4 deg. F.) by more than 1·7 deg. C. (3 deg. F.). The moist closet or room has a relative humidity of not less than 90 per cent.

The sand is natural silica sand from Ottawa, Ill., graded as follows: 98 per cent. retained on No. 100 sieve, 72 per cent. retained on No. 50 sieve, 2 per cent. retained on No. 30 sieve, none retained on No. 16 sieve. The moulding plaster added to provide the excess calcium sulphate conforms to Standard Specifications for Gypsum Moulding Plaster (C.59). Six specimens, three from each of two batches, are made for each cement.

The moulds are thinly covered with mineral oil, and the stainless steel or non-corroding metal reference points are set. A mixture of 3 parts of paraffin to 5 parts of resin by weight is heated to 110 to 120 deg. C. (230 to 248 deg. F.) and applied to the outside contact lines of the moulds to make them watertight.

The percentage of cement and gypsum plaster required to provide a mixture containing 7 per cent. SO_3 by weight is calculated as follows:

Percentage of cement, $\frac{(g-x)}{g-c}$ 100.

Percentage of gypsum moulding plaster, $\frac{(x-c)}{g-c}$ 100 where c is the percentage of SO_3 in the cement, g is the percentage of SO_3 in the gypsum, and x is the desired SO_3 content (per cent.).

The proportions of dry materials mixed at one time are 400 gr. of cement and plaster combined and 1,100 gr. of graded standard sand. The quantity of mixing water is as follows: with cements of Types I, II, IV, and V, 216 ml.; cements Types IA, IIA, 208 ml.; cement Type III, 224 ml.; cement Type IIIA, 216 ml.

The moulding plaster is hydrated for at least one hour before incorporating it in the mixture to avoid premature stiffening of the mortar; 150 ml. of water are placed in a 250-ml. beaker, the required amount of plaster is added, and stirred occasionally with a glass rod protected with a rubber "policeman." The slurry becomes creamy about 35 minutes after the plaster is added to the water; attention is required at this time to prevent the formation of lumps. With additional stirring the slurry becomes more fluid. The beaker is kept covered as much as possible to prevent loss of water by evaporation. Following hydration the plaster is transferred to the mixing bowl and the remaining mixing water used to wash the slurry from the beaker into the bowl.

The cement, the prehydrated plaster, and sand are mixed in accordancee with Section 5 of the Tentative Method for Mechanical Mixing of Hydraulic Cement Mortars of Plastic Consistency (C.305). Immediately after mixing the mould is filled in two layers, each compacted with the tamper. The mortar is worked into the corners, around the reference points, and along the surfaces of the mould with the tamper until a homogeneous specimen is obtained. After the top layer has been compacted, the mortar is cut off flush with the top of the mould and the surface smoothed with a few strokes of the trowel.

The specimens are cured in the moulds in the moist closet at 23 deg. C. (73.4 deg. F.) for 22 to 23 hours. They are then removed from the moulds, identified, and placed in water at 23 deg. C. for at least thirty minutes prior to making the initial length measurement 24 hours from the time the cement and water are mixed together.

After the bars have been removed from the moulds and measured, they are stored in water at 23 deg. C. The specimens are stored with at least $\frac{1}{4}$-in. clearance on all sides except for the necessary supports. The ratio of the volume of water to the volume of the bars must not exceed 5 to 1 to prevent excessive leaching. The water is replenished every seven days for the first 28 days and every 28-days thereafter.

The specimens are measured for length by means of the comparator described in A.S.T.M. Method C.151. The bars are wiped with a damp cloth before measuring.

If more than one bar is removed from the container at one time they are covered with a damp cloth to prevent evaporation of water.

The first measurement is made 24 hours from the time the cement and water are mixed. Additional readings are made at ages 7, 14, 21, and 28 days and every 28 days thereafter. The difference in length of specimens, when removed from the moulds at one day and any subsequent period, is calculated to the nearest 0·01 per cent. of the effective gauge length, and recorded as the expansion of the specimen at that period. The average expansion of the six specimens of a given cement represents the expansion of the cement at a given period.

The Density of Cement in Water.

A METHOD of ascertaining tne density of cement in water, which is claimed to be an improvement on the method recommended in the standard of the American Society for Testing Materials, is described in the Bulletin of the A.S.T.M. for July 1958 by Mr. C. L. Ford, formerly head of the analytical laboratory of the American Portland Cement Association. The procedure is described in the following. The apparent density of cement in water approximates more closely to the density of cement when in contact with water in concrete. (While not applicable to concrete, the density of cement in any other liquid may be obtained with modifications in converting weights to volumes.)

The apparatus used is (a) a vacuum pycnometer made by joining a 50-ml. Erlenmeyer flask to a stopcock of 6-mm. bore; high-vacuum stopcocks and high-vacuum lubricant are used throughout. To the other end of the stopcock is joined the inner part of a 14/35 ground-glass joint as shown in *Fig.* 1. At least three pycnometers should be available. (b) A connecting assembly consisting of the outer portion of a 14/35 ground-glass joint connected below a 100 ml. separating funnel with a small-bore inner tube to supply water to tne pycnometer, and a side-arm and three-way stopcock for connection to either a vacuum pump or to the atmosphere. (c) A water-trap in a Dewar flask filled about one-quarter full with methanol or ethanol, tnen with dry ice to about tnree-quarters full. The water-trap is inserted in the vacuum line between the three-way stopcock and the vacuum pump. (d) A funnel of 5 mm. outside diameter and a stem about 15 cm. long. (e) A vacuum pump (0.3μ or less of mercury).

The pycnometers must be clean and dry. Weigh the first pycnometer to the nearest milligramme and record this as the weight of the empty pycnometer. Connect the pycnometer to the vacuum apparatus. Close the stopcock of the separating funnel and open the three-way stopcock to the pump, start the pump, and evacuate for five minutes. Weigh the second pycnometer. Fill the separating funnel with freshly-boiled and cooled distilled water. At the end of the evacuation period, close the stopcock to the pump and open the stopcock to the separating funnel until the pycnometer is filled to a little above its stopcock. When effervescence of the water has nearly ceased, open the three-way stopcock

to the air, remove the pycnometer and, with the aid of a clamp, immerse it up to the stopcock for 30 minutes in a bath of constant temperature (preferably several degrees above room temperature) with the stopcock still open. Record the temperature of the water.

During the 30-minutes' period, proceed as before with the second and third pycnometers. At the end of the 30-minutes' period close the stopcock of the pycnometer, remove the pycnometer from the bath, and dry the outside.

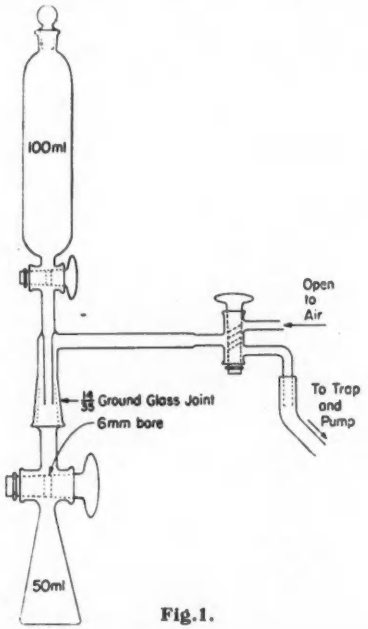


Fig.1.

Empty the excess water from the tube above the stopcock and dry the interior of the tube with absorbent tissue. Weigh and record the weight of the pycnometer plus water. Follow the same procedure with the second and third pycnometers.

After weighing, shake the water from the pycnometers, insert a small glass tube connected to the laboratory vacuum line, and draw air through until the pycnometer is dry (drying may be accelerated by rinsing the pycnometer once or twice with acetone before applying suction). Weigh the first pycnometer and record this as the weight of the empty pycnometer (this is a separate recording from that used in calibration). Weigh approximately 40 g. of cement. Clamp the pycnometer to a support stand and insert the funnel. Transfer the cement to the pycnometer, using a No. 16 bare copper wire to help to force the cement through the stem of the funnel. Weigh and record the weight of the pycnometer plus cement.

With the separating funnel stopcock closed and the connecting tube beneath it free of water, connect the pycnometer to the vacuum apparatus. Close the three-way stopcock to the vacuum pump and start the pump. Open the three-way stopcock cautiously to prevent drawing the cement out of the pycnometer flask; it is sometimes helpful also to tap the flask very lightly. Evacuate for 15 to 20 minutes for ordinary cements or 30 minutes for air-entrained cements. Weigh the second pycnometer, add cement, and weigh again.

At the end of the evacuation period, close the three-way stopcock to the pump and fill the pycnometer with water (if air bubbles appear the test must be repeated). Place in the constant-temperature bath for 30 minutes. Record the temperature of the water. Dry and weigh as previously described. Record the weight of the pycnometer plus cement and water. During the 30-minutes' period carry on the procedure as described with the second and third pycnometers.

Clean the pycnometers as soon as possible after the weights with cement and water are obtained. If the cement is allowed to set, the pycnometers will be ruined. The cleaning may be done as follows. Invert the pycnometer with the stopcock open, shake out some of the water, close the stopcock, shake until all the cement is loosened from the bottom, open the stopcock, and shake out as much of the slurry as possible. Insert a small glass tube connected to a water-line (the same tube that was used for drying), turn on the water, and flush well. Shake out the water, then, with the aid of the funnel, partially fill it with dilute hydrochloric acid (1–1), shake and empty. Rinse first with mains water injected through the glass tube, then with distilled water. Dry as previously described.

Calculate the density of the cement according to the following sample calculations.

DETERMINATION OF VOLUME OF PYCNOMETER.—(1) Weight of pycnometer filled with water, 170·045 g. (2) Weight of pycnometer empty, 115·205 g. (3) Weight of water to fill pycnometer (item 1—item 2), 54·840 g. (4) Temperature of water, 28·5 deg. C. (5) Specific volume of water, 1·00390 ml. per g. (6) Volume of pycnometer (item 3 × item 5), 55·054 ml.

DETERMINATION OF DENSITY OF CEMENT IN WATER.—(7) Weight of pycnometer empty, 115,204 g. (8) Weight of pycnometer + cement, 155·217 g. (9) Weight of pycnometer + cement + water, 197.526 g. (10) Temperature of water, 28·5 deg. C. (11) Weight of cement (item 8—item 7), 40·013 g. (12) Weight of water (item 9—item 8), 42,309 g. (13) Specific volume of water, 1·00390 ml. per g. (14) Volume of water (item 12 × item 13), 42·474 ml. (15) Volume of pycnometer empty (item 6), 55·054 ml. (16) Volume of cement (item 15—item 14), 12·580 ml. (17) Density of cement (item 11 — item 16), 3·181 g. per ml.

Stabilised Tristrontium Silicate.

IN "Zement-Kalk-Gips" for October, 1957, Mr. A. Braniski describes the preparation and the hydraulic behaviour of pure and stabilised tristrontium silicate.

Pure tristrontium silicate was prepared from an intimate mixture of strontium carbonate and finely-ground quartz powder in stoichiometric proportions. The mixture was burnt at 1580 to 1600 deg. C for five hours, ground, burnt again at the same temperature and the process repeated several times. Also it was burnt for five hours at the same temperature and then fused in an oxy-hydrogen flame. The product crumbled rapidly into a white powder which set weakly two hours after gauging with water, but under water its strength gradually disappeared.

Adulterated tristrontium silicates were prepared by the same burning processes, using a similar mixture of strontium carbonate and quartz powder containing respectively 3 per cent. of $Ca_3(PO_4)_2$, 2 per cent. of Al_2O_3 with 2 per cent. of Fe_2O_3 and 5 per cent. of natural serpentine, the percentage analysis of which was SiO_2, 35·45; Fe_2O_3, 9·43; Al_2O_3, 0·48; MgO, 36·14; H_2O, 18·56. These products no longer fell to powder, and when finely ground and gauged with water set well after about an hour, and the strength was unimpaired by immersion in water. Microscopic examination showed that hydration of the stabilised tristrontium silicate produces first a distrontium hydrosilicate with strontium hydroxide and then monostrontium hydrosilicate with further strontium hydroxide.

It is concluded that tristrontium silicate occurs in at least two forms, namely an hydraulic form stable at high temperatures and a non-hydraulic form stable at low temperatures. In the pure state the high-temperature form transforms rapidly at room temperature to the low-temperature form, with a considerable increase in volume, but it is stabilised by the presence of certain foreign ions. There is a close analogy with the case of β-dicalcium silicate and γ-dicalcium silicate. Distrontium silicate and monostrontium silicate were also prepared by both methods of burning, using intimate mixtures of strontium carbonate and finely-ground quartz in the appropriate stoichiometric proportions. These compounds do not occur in more than one form and do not crumble spontaneously. Only the distrontium silicate set when gauged with water.

Cement Works for Ghana.

An agreement has been signed between the Government of Ghana and the Tunnel Portland Cement Co., Ltd., for the construction of a cement plant at Takoradi at an estimated cost of £600,000. The equipment is to be supplied and installed by Messrs. F. L. Smidth & Co., Ltd. A new wharf is to be built at Takoradi at a cost of about £400,000 at which ships will discharge the clinker; the plant is expected to produce between 100,000 tons and 125,000 tons of cement a year, or nearly one-third of the country's requirements.

The Use of Pulverised-Fuel Ash as an Aggregate.

THE results of a Polish investigation of the properties of concrete made with pulverised-fuel ash in place of normal aggregates are described by Mr. S. Mazur in a recent number of " Materialy Budowlane", from which the following notes are abstracted.

COMPOSITION OF FUEL ASH.—X-ray photographs of ashes from various sources differ only in the density of the shadows. The lines are difficult to detect, and are visible only for small angles of refraction. This may be caused by a large percentage of amorphous substances as well as by poor crystallisation. It can be assumed that silica is present in the form of quartz, but no indication was found of its presence in the form of tridymite.

The effect of heating for twenty-four hours at temperatures of 1000, 1200, and 1300 deg. C. was studied. Slight fusing was observed at 1000 deg. C. and melting began at 1200 deg. C.; at 1300 deg. C. the ash became charred into a hard porous mass. Alternate cooling and heating was then applied, the rate of cooling being varied from several hours to two or three seconds. X-ray photographs showed that all the specimens had the same pattern of lines irrespective of the heat treatment applied, but deeper shadows were observed in the case of rapidly cooled ashes.

Ashes which had been heated were then finely ground, and, after the addition of 20 per cent. of hydrated lime, small cubes (about $\frac{7}{8}$ in.) were made to determine the setting properties. Ashes which had been heated to 1000 deg. C. had much lower crushing strengths than unheated ashes; those heated to 1300 deg. C. had no setting properties at all.

Deviations from the ideal crystalline composition may be caused by the lack of symmetry of certain particles, due to polarisation and thermal shrinkage, or to local dislocations of the crystalline structure caused by foreign bodies. Heating to temperatures greater than 900 deg. C. improves the crystalline structure and reduces the chemical activity. It has also been shown that the chemical activity of some ashes is increased after passing through grinding machines.

CRUSHING STRENGTH OF CONCRETE.—A constant water-cement ratio of 0.288 was used throughout. Cylinders about $3\frac{1}{8}$ in. in diameter and rectangular specimens about $1\frac{1}{2}$ in. square and $6\frac{1}{4}$ in. long were tested; all the specimens were consolidated by hand, cured in water for six, 24, or 48 hours, heated to a temperature between 40 and 50 deg. C. for four to six hours, and then steam-cured at 85 to 95 deg. C. for eight to twelve hours, the times depending on the size of the specimen. They were then stored in a damp atmosphere and finally tested at a temperature between 18 and 22 deg. C.

The results of tests on concrete composed of pulverised-fuel ash and ordinary Portland cement, and cured as described in the foregoing, are shown in *Fig.* 1. The rate of change of strength is also shown; this is appreciable for periods up to 90 days, after which a temporary fall of about 15 per cent. occurs, succeeded by a slow increase for 12 to 18 months. The results at 90 days are therefore more

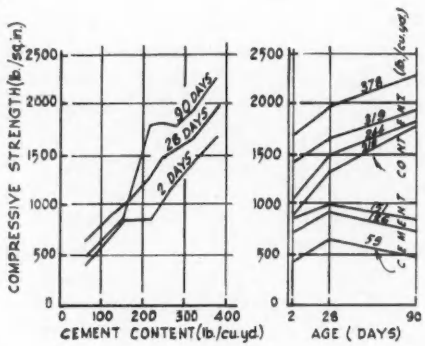


Fig.1.

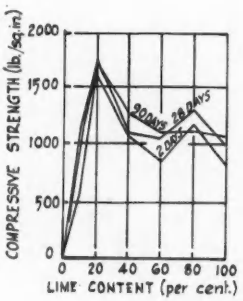


Fig.2.

reliable than those at 28 days. When the cement content is less than 168 lb. per cubic yard the strength at 90 days is less than that at 28 days, whereas when the cement content exceeds 200 lb. per cubic yard the strength increases steadily.

The results of tests on specimens made with lime instead of Portland cement are shown in *Fig.* 2. These show that the differences in strength after two, 28, and 90 days are negligible, and that the strongest concrete is obtained when the lime content is 20 per cent. (about 280 lb. per cubic yard).

SHRINKAGE AND EXPANSION.—Shrinkage and expansion varied according to the method of curing, and the content of cement or lime. Test values ranged from an expansion of 0·75 per cent. for steam-cured specimens made with Portland cement to a shrinkage of 10 per cent. in the case of specimens made with lime and not steam-cured.

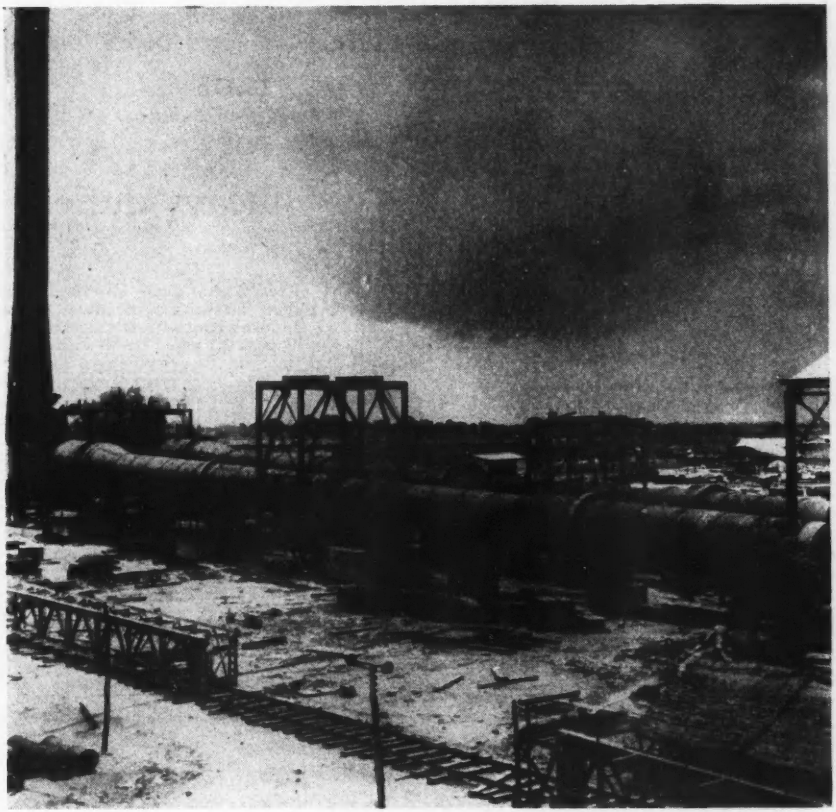
RESISTANCE TO FROST.—After 25 cycles of freezing and thawing no major spalling or cracks occurred. Superficial spalling to a depth of not more than $\frac{3}{8}$ in. occurred in places; the extent of the damage was inversely proportional to the cement content, and specimens containing lime suffered greater damage than those containing cement.

PERMEABILITY.—Permeability was greater in the case of specimens containing lime than in those containing cement. Values between 15 and 35 per cent. by weight were obtained.

FIRE RESISTANCE.—Resistance to fire was good.

Cement Production in Iran.

It is anticipated that by the end of the year 1959 there will be nine cement works in operation in Iran, with a total capacity of 650,000 tons a year. It is expected that this will exceed the consumption in Iran.



UTTAR PRADESH CEMENT WORKS

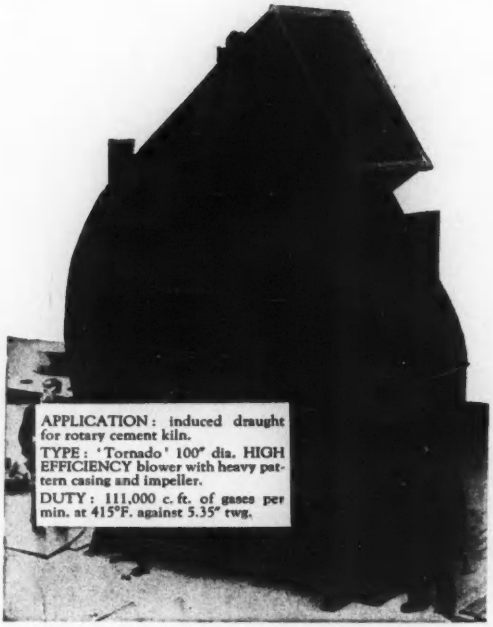
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The Reaction of Calcium Hydroxide, Silica Gel, and Water.

A THERMOCHEMICAL investigation of the reaction of calcium hydroxide, silica gel, and water, by Mr. Edwin S. Newman, is reported in the " Journal of Research " of the U.S.A. National Bureau of Standards for September 1957.

In the course of an introductory note the author states that the reactions of lime with silica and water are of fundamental importance in the study of the hydration of Portland cement, and are of particular interest in the study of the effect of pozzolanas. The energy changes occurring control the direction and extent to which the reactions may proceed, and a knowledge of these changes will aid in elucidating the mechanism of the process.

Measurements of the heat of reaction of lime with silica and water are in three general classes: (1) Determination of the heat of hydration of Portland cement; (2) determination of the heat of hydration of the separate compounds occurring in cement; and (3) measurement of the heat of reaction between calcium hydroxide solutions and silica gel. The heat-of-solution method of determining the heat of hydration of Portland cement, has resulted in an acceptance test for use when it is important to limit the heat evolved during the setting of concrete. Other investigators have measured the heat of hydration by direct methods, which are, however, limited to relatively short periods. The results of measurements in group (1) are useful for control and have been extended to determining the contribution of the separate constituents of cement to the heat of hydration. The direct measurements have been useful in explaining the important reactions that occur in the early stages of the setting of concrete.

The measurements of the heat of hydration of the compounds of Portland cement have almost without exception been made by the heat-of-solution method. Many of these measurements were made with pastes of hydraulic material and water having proportions and consistencies similar to those used in placing or testing Portland cement. The heats of reaction obtained have been used to aid in the identification of the reaction products. The third class of measurements, also made by the heat-of-solution method, have been made on the products obtained by the reaction between calcium hydroxide solution and silica gel performed in such a manner that a large quantity of solution came into contact with a small quantity of silica gel. These measurements also have been used to aid in identifying the products of the reaction.

The present report describes the results of heat-of-solution measurements made at intervals over an extended period on pastes of calcium hydroxide, water, and silica gel. The constituents were finely divided and in intimate contact with one another and with the small amount of water, so that local depletion of the calcium hydroxide in solution might be avoided. These measurements should agree with those made in class (3) and, together with those of classes (2) and (3), should provide data for calculating the heats of formation of the products of reaction.

The following summary is given of the results of the investigation. The heat

of the reaction $Ca(OH)_2 + SiO_2 \cdot nH_2O = CaO \cdot SiO_2 \cdot nH_2O$ is about 10·3 kcal., of which about 5 kcal. are the heat of wetting of the reaction product. The heat of the reaction

$$CaO \cdot SiO_2 \cdot nH_2O + mCa(OH)_2 = (1 + m)\, CaO \cdot SiO_2 \cdot (n + m)HO_2$$

is about 1·6 kcal. per mole of added $Ca(OH)_2$.

Calcium hydroxide reacts with silica gel and water in pastes at room temperature to form hydrated calcium silicate with a C/S ratio as high as 1·5. Above that ratio the $Ca(OH)_2$ is less firmly bound so that its presence is revealed by differential thermal analysis, although heat of reaction per molecule of silica continues to increase. Continued changes in the paste with time and with C/S ratio are indicated by changes in the behaviour of the heated pastes in the DTA furnace at temperatures above 800 deg. C.

Drying experiments indicated that the non-evaporable water remaining in the pastes was less than that equivalent to the CaO on a 1 : 1 molar basis. Above a C/S ratio of 1·5 the compositions of the dried pastes corresponded to the formula $[3CaO \cdot 2SiO_2 \cdot 2H_2O]\, [Ca(OH)_2]_x$.

Proposed new Cement Works in the Phillipine Islands.

The Government of the Phillipine Islands has provisionally approved a proposal of the Mindanao Portland Cement Corporation to build a cement works at Iligan at a cost of 3,200,000 U.S. dollars.

Production of Cement in the Dominican Republic.

In the year 1957, some 280,400 tons of cement were produced in the Dominican Republic, of which 70,000 tons were exported; the capacity of the cement works is 300,000 tons a year.

New Cement Works in Honduras.

A new cement works at Rio Bijao, near San Pedro Sula, is now in production. The works is owned by Cementos de Honduras S.A., and the plant was supplied by the Allis-Chalmers Co., of Milwaukee, U.S.A. It is expected that this works will supply all the cement required in the country.

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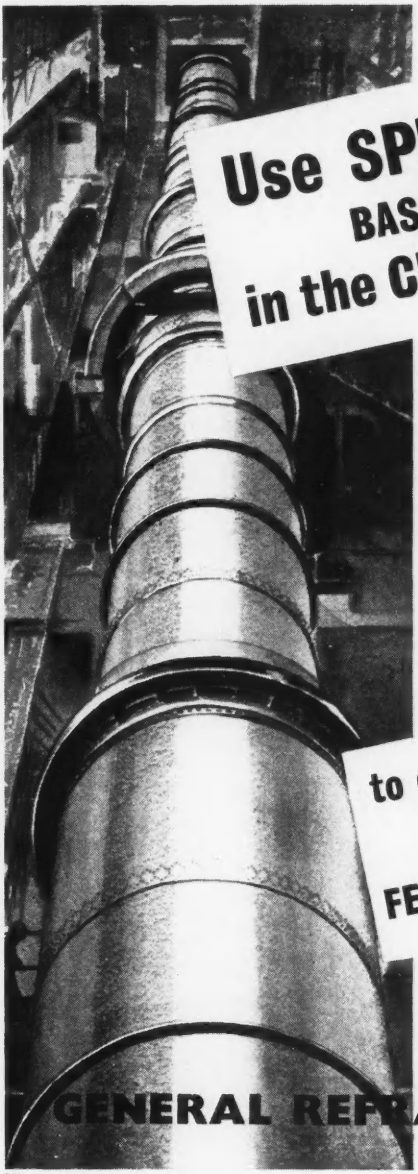
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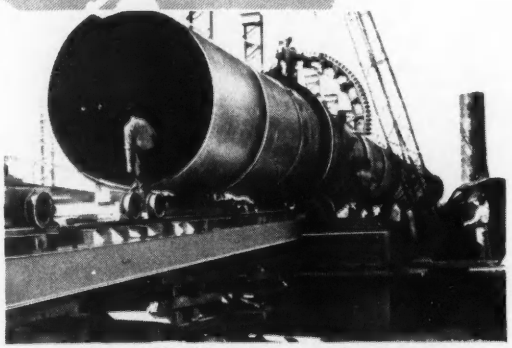
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